

Reply to “Comment on ‘X-ray resonant scattering studies of orbital and charge ordering in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ’ ”

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The interpretation given in our recent x-ray scattering study of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ in terms of charge and orbital ordering is questioned in the preceeding Comment by Garcia and Subias. They argue that anisotropy of the charge distribution induced by local distortions gives rise to the so-called charge order reflections. In this Reply we suggest that the two different pictures are reconcilable.

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In their Comment,^{1,2} García and Subías discuss the resonant scattering observed in the vicinity of the Mn *K* edge in the doped manganites, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, as arising from ordered local distortions of the oxygen octahedra around the Mn sites (see also Ref. 3). They make a number of points which we address in detail below. We should point out, however, that we believe the substance of their Comment is qualitatively consistent with the picture presented in Ref. 2. In particular, we believe that in such a scenario of ordered oxygen distortions, the Mn valence would also be modulated, with the same periodicity, as a result of the varying overlap with oxygen orbitals. In this sense the two pictures are reconcilable.⁴ Here, the charge ordering involves a non-integer valence modulation rather than the nominal $\text{Mn}^{3+}/\text{Mn}^{4+}$ ordering. This is consistent with the x-ray data as was pointed out in the original paper.²

The main points of the Comment are as follows. First, it has long been known that anisotropies of the resonant site can give rise to resonant scattering at forbidden reflections. This is true, of course, and it is referred to in our paper under the generally accepted term of Templeton scattering.

Second, that the scattering factor (form factor) is a tensor on resonance. This is also true, and discussed at length in our paper. However, at one point in the paper we simplified to a scalar model in order to model the energy dependence of the “charge-order” reflection (this energy dependence does not depend strongly on the tensorial character of the scattering). It is this assumption to which the authors of the Comment appear to object most strongly. Our use of this model is carefully qualified in the text. In particular, the model is not intended to reproduce the azimuthal dependence—and it explicitly cannot. In addition, the authors dispute the “reported” energy dependence of the Mn scattering factors. Here again their objection goes beyond what was intended in

our paper. The model contained generic features intended to illustrate such effects as the change in sign of observed interference oscillations with increasing momentum transfer. It was not meant to represent the detailed response of Mn (as was also pointed out in the paper).

In order to address this point and to put this approach on a more quantitative footing, we have taken x-ray absorption data at the Mn *k*-edge, on the $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ sample at room temperature. These data measure the (average) resonant factors of the Mn sites and allow one to extract f' and f'' for the Mn ion in this structure (Fig. 1). With these and the atomic positions, one can model the energy dependence of the resonant scattering in a more direct manner. In Fig. 1, we have taken the refined positions for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (Ref. 5) as a reasonable guess for the crystal structure (other refinements were also tried and are discussed in Ref. 6). The (010) charge order peak was then simulated by assuming a rigid 1 eV shift (in opposite directions) for the resonant scattering factors of the two inequivalent sites, relative to their high temperature values. As is seen from the figure, the agreement is quite good, confirming the validity of this approach. The shift, which is smaller than that expected from full integer valence separation must lie in the 4*p* levels (and not the 1*s*) to provide the anisotropy required to explain the observed azimuthal dependence. The combination of this small shift and the anisotropy, which even single crystal x-ray absorption measurements will average over, further reducing the size of any effect, explains why such measurements do not distinguish the two sites. As discussed at length in a forthcoming paper,⁶ the azimuthal dependence for this reflection is of the form $1 + 2 \sin^2 \psi + \sin^4 \psi$ consistent with experimental observations.

The third point made in the Comment was that the interpretation of integral $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordering is inconsistent with the interpretation of x-ray absorption near edge

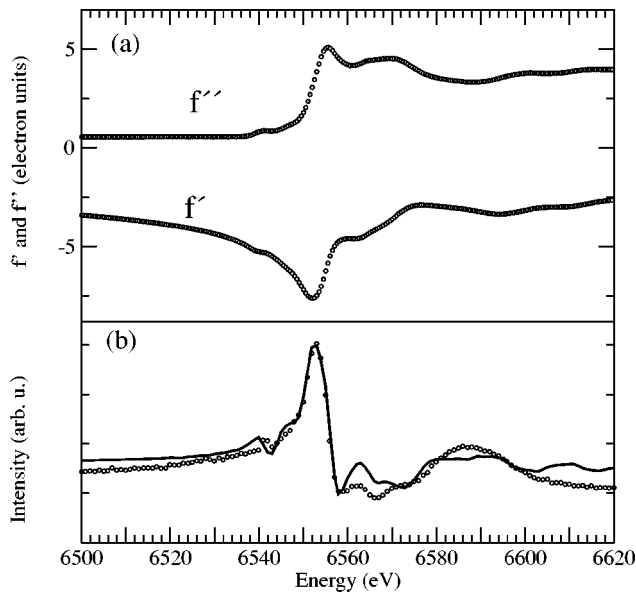


FIG. 1. (a) Real (f') and Imaginary (f'') parts of the resonant scattering factors as calculated from a XANES spectrum. (b) (solid line) Simulation of the (010) reflection using the experimental resonant factors f' and f'' compared to the experimental resonant spectrum of the (010) reflection (open circles).

structure (XANES) measurements.^{7,8} This has already been discussed above and was addressed in our paper where we noted that the scattering data did not require full valence separation. Here it is important to note that nonintegral charge disproportionation (i.e., $\text{Mn}^{3.5+\delta}$, $\text{Mn}^{3.5-\delta}$) is *not* inconsistent with the XANES data (again see above and Ref. 8) and is consistent with the x-ray scattering data.⁶

Fourthly, the authors stated that their model requires only anisotropy around the Mn ions to reproduce the azimuthal and polarization dependence of our data. However, the authors do not make the case that there is anisotropy and *no* disproportionation. It seems likely that any anisotropy would be accompanied by some level of charge disproportionation

as a result of the differing bond lengths, as pointed out above, and thus at root their model is consistent with ours.

The fifth point was that the difference in the peak widths (correlation lengths) of the two types of reflections may be explained by antiphase domains of misoriented distortions. This mechanism is equivalent to the one put forth in Ref. 2. A direct implication of our model of misoriented orbitals is misoriented distortions.

Finally, it was argued that the ordered patterns proposed in Ref. 2 are inconsistent with the number of electrons given by the nominal doping for the $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and the $\text{Pr}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ samples. *A priori* there is no reason to rule out charge ordering based on this difference in the number of valence electrons. Several possible models were discussed in our paper in which the extra electrons could be accommodated without breaking the coherence of the charge order.² This question will also be taken up again in a forthcoming publication.⁶

In summary, we believe that a model of charge and orbital ordering with a CE-type pattern is appropriate for $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$. Further, it appears that the charge disproportionation is incomplete and the resonant intensity derives largely from the oxygen distortions. In this, we believe that our view and that of Garcìa and Subías are equivalent and are consistent with existing data such as XANES and neutron scattering studies of the magnetic order. However, understanding the details of exactly where the charge resides and the driving mechanism behind this ordering are subtle questions that will require, as urged by Garcìa and Subías, detailed analysis of azimuthal, polarization, and energy dependence of the scattering combined with theoretical modeling with input from XANES data. Such studies should be able to significantly constrain models of the electronic and structural behavior of the half-doped manganites.⁶

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⁴Note, however, that these two pictures differ significantly from that of A. Daoud-Aladine *et al.* [Phys. Rev. Lett. **89**, 097205 (2001)], who argue that every Mn site has the same valence and have a different ordering of the inequivalent Mn sites. It does

not appear that this latter model can be reconciled with the other two, or with aspects of the experimental data.

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